

The Specific Heat at Constant Volume of *para*-Hydrogen at Temperatures from 15 to 90° K and Pressures to 340 atm

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THE computation of thermodynamic properties, relative to that of ideal gas, of compressed fluid by means of the equation of state data requires the data to be extremely accurate. The uncertainties that are introduced through the derivatives of the equation of state would be minimized by supplementing the calculations with the constant volume specific heat data of the compressed fluid. Specific heats for both ideal gas and compressed liquid states, together with *PVT* data, will permit computations around closed paths to check the overall consistency of the data. For these applications our current programme on hydrogen properties includes calorimetric specific heats of *para*-hydrogen at constant volume. There are reported in this paper measurements of C_v of the compressed fluid from well below to above the critical temperature.

Experimental procedure

The descriptions of apparatus and sample preparation have been published.^{1,3} The calorimeter consists of a spherical stainless steel sample container of 72 cm³ volume with a platinum resistance thermometer, heater windings, and difference thermocouples attached. The container was suspended by a filling capillary inside an adiabatic shell which in turn was mounted in a cryostat.

The hydrogen sample is 20° K equilibrium hydrogen prepared from electrolytic hydrogen as previously described.³ The chemical impurities present in the hydrogen sample are estimated to be less than 0.01 per cent based on tests made by the supplier (National Cylinder Gas Co.). The isotopic content is estimated from a knowledge of the process of preparation of the hydrogen gas to be the same as that of naturally occurring hydrogen. The *para*-hydrogen concentration at the beginning of a run is estimated to be in excess of 99 per cent, based on the iron oxide catalyst temperature and the indication from a thermal conductivity analyser. In preliminary studies the conversion rate of *para*- to *ortho*-hydrogen at pressures up to 300 atm was of the order of 1 per cent per day at 76° K.

The desired filling density was determined approximately from the *PVT* data of this laboratory.² The actual

amount of sample was measured at the end of each run by gasometry³ and this value was used in calculations of the density and the specific heats. An adjustment was made for the gas contained in the filling capillary. This adjustment, however, was extremely small and could have been neglected. Adjustment was also made for the change in volume with temperature and pressure. The maximum adjustment in density from all these sources during a run was less than 0.5 per cent. The true density associated with each specific heat value was thus calculated¹ from the actual amount of sample in the sample container, $V = V(T, P)$.

Heat capacity measurements were made as a function of temperature at nearly constant density. An adjustment was made to the measured value of specific heat \bar{C}_v , for the work done by the fluid as it expanded. This adjustment, developed by Walker,⁴ is

$$\Delta C_v = -\frac{1}{N} \left[T \left(\frac{\Delta P}{\Delta T} \right)_v + \frac{\Delta P}{2} \right] \frac{\Delta V}{\Delta T} \quad \dots (1)$$

ΔC_v is added to \bar{C}_v to obtain the adjusted value C_v . The calculated increase in pressure during the heating interval is ΔP , ΔV is the corresponding increase in volume, $(\Delta P/\Delta T)_v$ was calculated from *PVT* data, and N is the amount of sample in the container. This adjustment was always less than 1 per cent of the measured value.

The heat capacity of the sample was taken to be the difference between the total heat capacity and the heat capacity of the sample container. The adjustment for curvature was found to be negligible in these measurements. The heat capacity of the sample container was measured at 35 temperatures between 15 and 100° K and fitted with two polynomials by least squares. Below 26° K a polynomial of 6 terms was used and above 26° K a polynomial of 7 terms. The first and second derivatives of the two polynomials at 26° K agreed to within 0.03 per cent and the r.m.s. per cent deviation of the measured values from the polynomial representations was 0.12 per cent.

A platinum resistance thermometer, calibrated on the NBS-1955 temperature scale by the NBS Heat Division in Washington, D.C., was used to measure T and ΔT .

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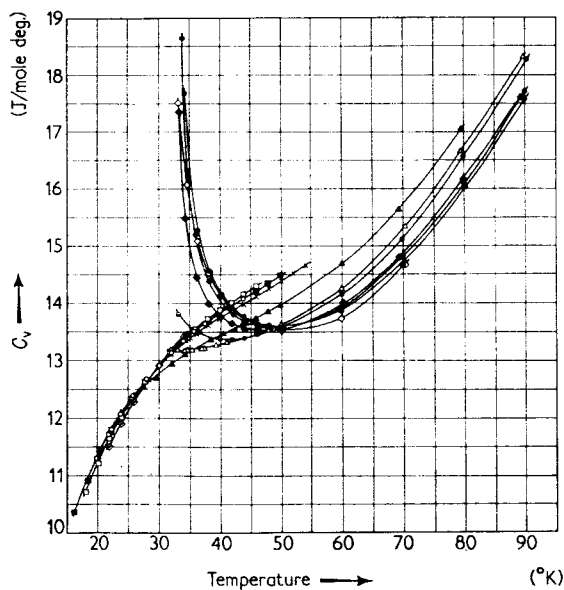
Table 1. Experimental Data. Specific Heat, Temperature, Density, and Pressure

T (°K)	C_v (J/mole deg.)	Density (mole/cm ³)	P (atm)		T (°K)	C_v (J/mole deg.)	Density (mole/cm ³)	P (atm)	
19-916	11-31	0-03788	49-76	Run 1	16-139	10-37	0-03790	23-70	Run 5
21-863	11-71	0-03787	67-81		18-404	10-92	0-03790	36-03	
22-377	11-80	0-03787	72-61		20-481	11-46	0-03789	55-15	
23-924	12-06	0-03786	87-03		22-038	11-74	0-03788	69-63	
25-930	12-39	0-03785	105-77		24-088	12-09	0-03787	88-75	
28-037	12-67	0-03784	125-48		26-136	12-41	0-03786	107-90	
30-060	12-92	0-03783	144-41		28-160	12-68	0-03785	126-84	
32-082	13-15	0-03782	163-29		30-196	12-92	0-03784	145-89	
34-056	13-35	0-03781	181-71		32-239	13-16	0-03783	164-98	
35-742	13-51	0-03781	197-41		34-255	13-37	0-03782	183-79	
37-538	13-65	0-03780	214-03		35-982	13-52	0-03781	199-85	
43-923	14-08	0-03777	272-42		37-951	13-69	0-03780	218-08	
					39-930	13-82	0-03780	236-43	
					41-911	13-95	0-03779	254-58	
33-889	18-64	0-01619	14-56	Run 2	43-900	14-08	0-03778	272-69	Run 6
36-035	15-21	0-01619	18-88		45-902	14-22	0-03777	290-82	
38-194	14-38	0-01618	23-28		47-938	14-35	0-03776	309-13	
42-244	13-81	0-01618	31-64		49-992	14-49	0-03776	327-42	
44-245	13-69	0-01618	35-79						
46-166	13-63	0-01618	39-78		33-107	13-19	0-02545	19-05	
49-986	13-61	0-01618	47-73		34-245	13-18	0-02545	23-96	
59-894	14-83	0-01617	68-32		34-622	13-20	0-02545	25-62	
69-931	13-92	0-01616	89-06		35-434	13-19	0-02545	29-13	
80-052	16-10	0-01615	109-80		36-926	13-21	0-02545	35-64	
89-943	17-70	0-01614	129-91		37-354	13-23	0-02545	37-51	
					39-301	13-28	0-02544	46-04	
					41-109	13-33	0-02544	53-96	
					45-860	13-45	0-02543	74-75	
20-140	11-34	0-03676	27-62	Run 3	47-949	13-55	0-02543	83-86	Run 7
22-205	11-80	0-03675	45-91		50-060	13-63	0-02542	93-05	
24-028	12-11	0-03674	62-16		59-845	14-25	0-02541	135-28	
24-182	12-13	0-03674	63-53		70-316	15-34	0-02539	179-75	
26-087	12-41	0-03674	80-54		79-472	16-65	0-02537	217-94	
28-132	12-67	0-03673	98-79		89-674	18-31	0-02535	259-83	
30-145	12-90	0-03672	116-74						
32-142	13-15	0-03671	134-52		27-532	12-55	0-03072	11-03	
34-124	13-30	0-03670	152-14		29-628	12-70	0-03072	24-44	
36-050	13-48	0-03669	169-18		32-215	12-95	0-03071	40-97	
37-971	13-63	0-03668	186-11		34-262	13-12	0-03070	54-04	
39-944	13-76	0-03668	203-41		36-344	13-26	0-03070	67-30	
41-916	13-87	0-03667	220-59		38-439	13-37	0-03069	80-57	
43-909	14-00	0-03666	237-85		40-505	13-47	0-03069	93-60	
45-923	14-12	0-03665	255-17	Run 4	42-494	13-54	0-03068	106-09	Run 8
47-978	14-26	0-03664	272-73		43-881	13-64	0-03068	114-75	
50-029	14-39	0-03664	290-16		45-898	13-74	0-03067	127-31	
52-051	14-52	0-03662	306-98		47-880	13-86	0-03067	139-58	
54-085	14-67	0-03662	324-33		49-879	13-97	0-03066	151-89	
					60-070	14-69	0-03063	213-71	
18-021	10-73	0-03936	70-88		69-365	15-63	0-03061	268-76	
20-048	11-23	0-03935	90-41		79-554	17-04	0-03058	327-68	
21-999	11-66	0-03934	109-45						
23-985	12-02	0-03933	129-00		33-497	17-56	0-01095	13-25	
25-963	12-36	0-03932	148-56		34-695	16-07	0-01095	14-77	
27-931	12-64	0-03931	168-05		36-367	15-09	0-01095	16-87	
29-909	12-90	0-03930	187-65		38-150	14-52	0-01095	19-09	
31-907	13-14	0-03929	207-42		40-105	14-14	0-01095	21-51	
33-907	13-36	0-03928	227-23		42-325	13-88	0-01095	24-25	
35-894	13-57	0-03927	246-87		44-538	13-69	0-01095	26-98	
37-971	13-74	0-03926	267-28		46-624	13-61	0-01094	29-54	
39-935	13-88	0-03925	286-47		48-607	13-56	0-01094	31-97	
41-897	14-02	0-03924	305-56		50-555	13-57	0-01094	34-36	
43-899	14-16	0-03924	324-96		59-757	13-77	0-01094	45-59	
45-915	14-31	0-03923	344-48		70-241	14-68	0-01094	58-30	

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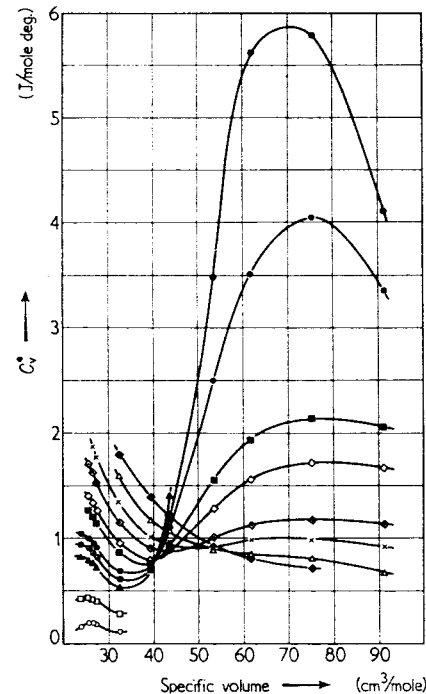
Table 1—continued

T (°K)	C_v (J/mole deg.)	Density (mole/cm ³)	P (atm)		T (°K)	C_v (J/mole deg.)	Density (mole/cm ³)	P (atm)	
33-316	17-36	0-01869	13-60	Run 9	21-991	11-52	0-04181	198-83	Run 11
34-425	15-47	0-01869	16-28		23-917	11-91	0-04180	219-32	
36-217	14-46	0-01869	20-71		25-987	12-29	0-04179	241-49	
38-159	14-01	0-01868	25-60		28-055	12-62	0-04177	263-73	
40-040	13-78	0-01868	30-39		30-055	12-91	0-04176	285-30	
41-969	13-66	0-01868	35-33		32-046	13-18	0-04175	306-77	
44-018	13-57	0-01868	40-59		33-990	13-41	0-04174	327-74	
46-142	13-55	0-01868	46-06						
48-238	13-54	0-01868	51-47		34-216	17-67	0-01329	14-72	Run 12
50-249	13-57	0-01867	56-66		36-402	15-27	0-01329	18-19	
60-335	14-01	0-01866	82-68		38-384	14-56	0-01329	21-32	
69-404	14-81	0-01866	105-92		40-214	14-15	0-01329	24-22	
79-924	16-18	0-01864	132-60		42-107	13-92	0-01329	27-21	
89-331	17-59	0-01863	156-24		43-985	13-77	0-01329	30-18	
					45-940	13-68	0-01329	33-27	
					47-994	13-61	0-01329	36-52	
33-696	13-81	0-02291	16-97	Run 10	50-057	13-60	0-01328	39-78	
35-943	13-51	0-02291	24-84		59-868	13-88	0-01328	55-24	
40-010	13-38	0-02291	39-39		69-974	14-68	0-01327	71-10	
41-943	13-38	0-02290	46-36		80-206	16-03	0-01327	87-01	
43-900	13-39	0-02290	53-43		90-055	17-57	0-01326	102-24	
45-976	13-45	0-02290	60-94						
48-043	13-49	0-02290	68-41						
50-086	13-59	0-02289	75-79						
60-017	14-15	0-02288	111-49						
69-823	15-10	0-02287	146-33						
79-870	16-55	0-02285	181-51						
90-319	18-26	0-02283	217-63						



- | | | |
|------------|------------|-------------|
| 1 0-0378 ○ | 5 0-0378 ■ | 9 0-0186 ◆ |
| 2 0-0162 ● | 6 0-0254 △ | 10 0-0229 ⊙ |
| 3 0-0367 × | 7 0-0306 ▲ | 11 0-0417 ◇ |
| 4 0-0393 □ | 8 0-0109 ◇ | 12 0-0132 ⊕ |

Figure 1. Specific heat as a function of temperature for several densities. The run numbers are given above and the densities are in mole/cm³



- | | | | |
|---------|---------|---------|---------|
| 28° K ○ | 30° K □ | 33° K ▲ | 34° K ⊙ |
| 35° K ● | 38° K ■ | 40° K ◇ | 45° K ◆ |
| 50° K × | 60° K △ | 75° K ◆ | |

Figure 2. Residual specific heat as a function of specific volume for several temperatures

Experimental results

Table 1 lists the adjusted values of the specific heat of *para*-hydrogen. The temperature is the average of the sample container temperatures which were measured before and after the heating interval and extrapolated to the middle of the heating time interval. Figure 1 shows the specific heat as a function of temperature for each run.

Figure 2 shows the residual specific heat versus specific volume for several isotherms. The residual specific heat is defined as

$$C_v^*(v, T) = C_v(v, T) - C_v^\circ(T) \quad \dots (2)$$

where $C_v^\circ(T)$ is the 'ideal gas' value.⁵ This residual arises from molecular interaction. The high maximum in the 34° K isotherm occurs approximately at the critical volume, as expected. The spacing of the data in density precludes locating this maximum accurately. An interesting feature of this surface is another maximum at low specific volume. The suggested shape of a general $C_v^*(v, T)$ surface due to Rowlinson,⁶ based on measurements of several authors, does not have this last feature. At large values of the volume, C_v^* approaches zero as v increases, since the real gas properties approach the ideal at low density.

Analysis of results

The values of C_v have an estimated uncertainty of 0.3 per cent below 50° K with the exception of the lower density runs 2, 8, 9, and 12 where the uncertainty may be as large as several per cent near the critical temperature. The uncertainty in C_v in the region above 50° K may be as large as 0.5 per cent.

The ratio of the sample heat capacity to the gross heat capacity varies from 0.94 at the low temperature, high density case to 0.28 at the high temperature, low density case.

The reproducibility of the data is indicated by runs 1 and 5 for which the filling conditions were duplicated. The agreement, in this somewhat favourable case, in C_v from the two runs is within 0.2 per cent.

A test of the capability of the calorimeter was made by measuring the specific heat of solid argon and comparing the results to the extensive data of Flubacher, Leadbetter, and Morrison.⁸ Both sets of data were smoothed and the percentage difference was computed at every 5° K from 20 to 60° K. The r.m.s. percentage difference was 0.35 per cent. The measurements of this laboratory on solid argon were reported in reference 1.

The residual specific heat may be also calculated from *PVT* data according to the relation⁶

$$C_v^*(v, T) = T \int_{\infty}^v \left(\frac{\partial^2 P}{\partial T^2} \right)_v dv \quad \dots (3)$$

The *PVT* data on *para*-hydrogen of this laboratory are not yet in final form to carry out this calculation to compare

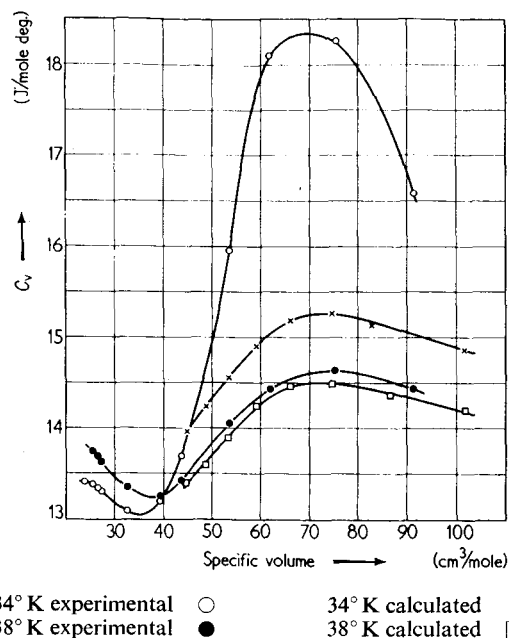


Figure 3. Comparison of specific heats calculated from *PVT* data and specific heats measured directly by calorimetry

with that obtained calorimetrically. Obviously great care must be taken with the representation of the *PVT* data if the second derivative in equation (3) is to be reliable. Preliminary comparison was made at a few points using the *PVT* data for normal hydrogen.⁵ An equation equivalent to equation (3) using the smoothed values of $(\partial Z/\partial T)_v$ and $(\partial^2 Z/\partial T^2)_v$, where $Z = PV/RT$, was used. The 'ideal gas' values for *para*-hydrogen were used for $C_v^\circ(T)$. The results for the 34 and 38° K isotherms are shown with the measured values of C_v in Figure 3. The agreement is quite reasonable, with most of the disagreement due to uncertainties in the derivatives of Z . For the 34° K isotherm,

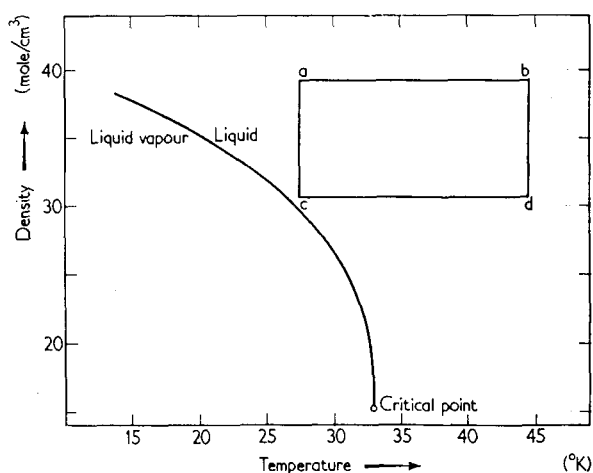


Figure 4. Path of integration for entropy calculations

which is only slightly above the critical temperature, some of the disagreement may be due to non-equilibrium experimental conditions. Equilibrium in the region of the critical point is known to be sluggish. Large deviations near the critical density as seen in Figure 3 have also been observed in carbon dioxide in the work of Michels and Strijland.⁷

A check on the internal consistency of the C_v and PVT measurements was made by calculating the entropy changes in a closed loop consisting of two isochores and two isotherms as shown in Figure 4. The entropy change along an isotherm was calculated by numerically integrating $(\Delta P/\Delta T)_v$ with respect to specific volume. The quantity $(\Delta P/\Delta T)_v$ is approximated from a preliminary smoothing of the PVT data of this laboratory. The change in entropy along an isochore was calculated by integrating smoothed values of C_v/T . The results, which indicate good internal consistency, are summarized in Table 2.

The densities and pressures listed with the values of specific heat are accurate to within 1 part in 500.

This report represents part of a programme on thermodynamic properties of *para*-hydrogen under the direction of R. D. Goodwin. Acknowledgement is made to R. D. Goodwin, L. A. Weber, and H. M. Roder who have made numerous experimental and computational contributions. This work was supported by the U.S. National Aeronautics and Space Administration.

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Table 2

Path	ΔS (J/mole deg.)
a to b	6.012
b to d	5.602
d to c	-5.870
c to a	-5.757
Total	-0.013